Monte Carlo Simulations of Zeolites

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Recent high-resolution nuclear magnetic resonance measurements have led to the accurate determination of the nearest-neighbor distributions of silicon among sites having 0–4 aluminum nearest neighbors as calculated by Monte Carlo simulations, for the 2-D square and the 3-D diamond lattices for different Si:Al ratios. The empirical Lowenstein's rule, which excludes the possibility of alumina as nearest neighbors, is imposed. The comparison between the theoretical and the experimental results (ZK4 and Faujasite) shows that while Lowenstein's rule with nearest-neighbor Al–Al interactions can explain the data qualitatively, to obtain quantitative agreement with the experiments the introduction of next-nearest-neighbor Al–Al interactions is necessary. Our numerical simulations predict that the aluminum distribution is a function of the zeolite synthesis temperature, which offers a unique way of controlling the atomic distributions in zeolites.

Recent high-resolution nuclear magnetic resonance (NMR)[1-7] measurements have led to the accurate determination of the nearest-neighbor distribution of silicon and aluminum atoms in zeolites. Tetrahedrally coordinated silicon may bond to zero, one, two, three, or four O–Al groups in the zeolite framework leading in each case to a different chemical shift.

The purpose of this work is to calculate the distribution of the five type of chemically nonequivalent silicon for ZK4 and faujasites where the Al atoms are randomly distributed, consistent with the constraint of Lowenstein's rule[8] which prohibits alumina–alumina nearest neighbors. These distributions were calculated by Monte Carlo simulations for the two-dimensiona (2-D) square and three-dimensional (3-D) diamond lattices for different Si:Al ratio.

The structure of faujasite and ZK4 is very complicated. Like that of all zeolites, is built up of SiO_4 and AlO_4 tetrahedra linked by corner sharing. In order to explain the NMR data for the distribution of Al around a Si, it is necessary to retain only the basic characteristics of the real structure in our model. Since the Faujasites, as well as the ZK4, have four nearest neighbors (nn) atoms, we will consider simple binary alloy models with Si and Al as constituents. Since the number of nn is four, we used a 2-D square and a 3-D diamond lattice in our numerical simulations. From this study we hope to extract the basic underlying mechanism for explaining the distributions of Al around a Si.

Once the model is chosen, there are basically two ways that one can attack the problem of calculating the distributions, either analytically or numerically. Analytically one usually has to make many simplifying approximations in order to obtain any results, while in numerical simulations one loses the beauty of an analytical form for the distributions.

Analytical Method. Let us review briefly some ideas from probability theory that will be useful in understanding the results. Let $P(Al,1/Si,0) = p$ be the conditional probability, that site 0 is occupied by a Si and it has an Al nearest neighbor at site 1. Similarly, let $P(Al,1/Al,0) = q$, then it is easy to show that $P(Si,1/Al,0) = 1 - q$ and $P(Si,1/Si,0) = 1 - p$. Since we have a binary alloy with Al and Si as the only two constituents it is easy to show that

$$X_{Al} = X_{Si}P(Al,1/Si,0) + X_{Al}P(Al,1/Al,0) \qquad (1)$$

$$X_{Al} = X_{Si}p + X_{Al}q$$

where X_{Al} and X_{Si} are the concentration of Al and Si, respectively. $X_{Al} + X_{Si} = 1$. From eq 1 by defining $R = X_{Si}/X_{Al}$ we obtain

$$p = (1 - q)/R \qquad (2)$$

Note that given R and one of the conditional probabilities, all the other nn conditional probabilities are specified. To calculate the average number of Al around a given Si we define a quantity y_i

which is 1 if the nn i is Al and zero if the nn i is Si. We therefore have that

$$\langle Al \rangle = \sum_{i=1}^{4} \bar{y}_i = 4\bar{y}_i = 4P(Al,1/Si,0) = 4p = 4(1 - q)/R \qquad (3)$$

where $\bar{y}_i$ is the average value of y_i. Experimentally for most of the zeolites $\langle Al \rangle = 4/R$ which suggest that $q = P(Al,1/Al,0) \rightarrow 0$, i.e., no alumina–alumina nearest neighbors. This is commonly referred to as Lowenstein's rule.[8] Up to this point no approximations have been made; however, if we are interested for the distributions P_n ($n = 0, 1, 2, 3, 4$) of n Al around a given Si we need to make some approximations. Consider a site (call it 0) and its four neighbors (Figure 1). It is not necessarily true, for example, that

$$P(Al,2/Si,0;Al,1) = P(Al,2/Si,0) \qquad (4)$$

as there are many paths other than $1 \rightarrow 0 \rightarrow 2$ along which the atom at site 1 influences the atom at site 2. However, as a first approximation, we will nevertheless assume that eq 4 and its generalizations are approximately valid, in order to obtain a closed system for equations for the distributions P_n. Using a binomial probability distribution we can calculate the probabilities P_n that a Si has n Al and $4 - n$ Si nearest neighbors

$$P_n = \frac{4!}{n!(4 - n)!}p^n (1 - p)^n \qquad (5)$$

where $p = (1 - q)/R$ and $q = P(Al,1/Al,0)$. This result was also obtained by Mikovsky.[9] By letting $q = 0$ (Lowenstein's rule) one can compare the P_n's from eq 5 with the experimental results for faujasite, ZK4, and other zeolites. Although there is some agreement with the data, the overall agreement is not good. In some regions of R there are large differences between experiment and theory. Also since the results of eq 5 are the same for all the lattices that have four nn the role of dimensionality is probably

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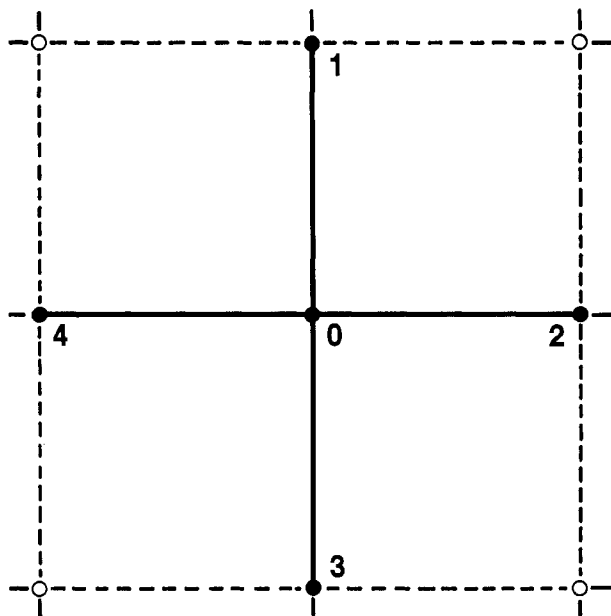[†] Present address: Department of Physics, Iowa State University, Ames, IA 50011.

Figure 1. A site 0 and its four nearest neighbors.

underestimated. Though it is possible to improve the theoretical results by going to next nearest neighbors (nnn), it is very difficult to obtain a self-consistent set of equations with all possible nnn probabilities. However, I will take a different approach here and carry out some Monte Carlo simulations for models of binary alloys to see if the probability distribution functions P_n can be improved. By using these numerical techniques, it is possible to include both nn and nnn interactions on any lattice structure of interest. Here we shall concentrate on the 2-D square and 3-D diamond lattice since they are both fourfold coordinated.

Numerical Simulations

Nearest-Neighbor Alumina-Alumina Repulsion. We first study a simple model for the binary Si:Al alloys in which the only interaction is a strong alumina-alumina nearest-neighbor repulsion. The Hamiltonian for this system is simply

$$H = -J_{Al,Al}\sum_{n,n}\delta_{n_i,Al}\delta_{n_j,Al} \tag{6}$$

where $J_{Al,Al} < 0$ is the repulsive nn Al–Al interaction. Here n_i = Al or Si and $\delta_{n_i,Al}$ is a Kronecker delta which is one if n_i = Al and zero if n_i = Si. The sum is over all nn pairs. We have taken the other two interactions $J_{Al,Si}$ and $J_{Si,Si}$ = 0 for convenience. In order to satisfy Lowenstein's rule we will always choose the Al–Al interaction, $|J_{Al-Al}|$ much larger than K_BT, the thermal energy. In the limit $|J_{Al,Al}| \rightarrow \infty$, there are no Al–Al nearest neighbors in the final equilibrium configuration. It is easy to convince oneself that the number of Al–Al nn $N_{Al-Al} = 0$, the other energies J_{Al-Si} and J_{Si-Si} have no effect on the final distribution. This is because, for $N_{Al-Al} = 0$, the number of nearest neighbors $N_{Al-Si} = pN$ and $N_{Si-Si} = (1-p)N$. The distributions P_n then become independent of J_{Al-Si} and J_{Si-Si}. This is equivalent with the argument we presented above that, given the ratio Si:Al and one of the conditional probabilities, then all the other nn conditional probabilities are specified.

Since this limit is basically athermal, one might think that the distributions P_n could be simple to calculate. One simple way, for instance, would be to use zero temperature Monte Carlo. This is a rather simple procedure where we start with a lattice and randomly fill up the lattice sizes with Si and Al atoms in the desired concentration ratio R. Since some Al will be nn of other Al, this random state will of course be far from the ground state. However, the energy can be lower by simply going through the lattice interchaning any pair of Al–Si atoms which reduce the number of Al–Al nn pairs. One would hope to eventually find a good configuration with $E = 0$, i.e., $N_{Al-Al} = 0$. While this works satisfactory for small X_{Al}, the system gets hung for $X_A \geq 0.40$.
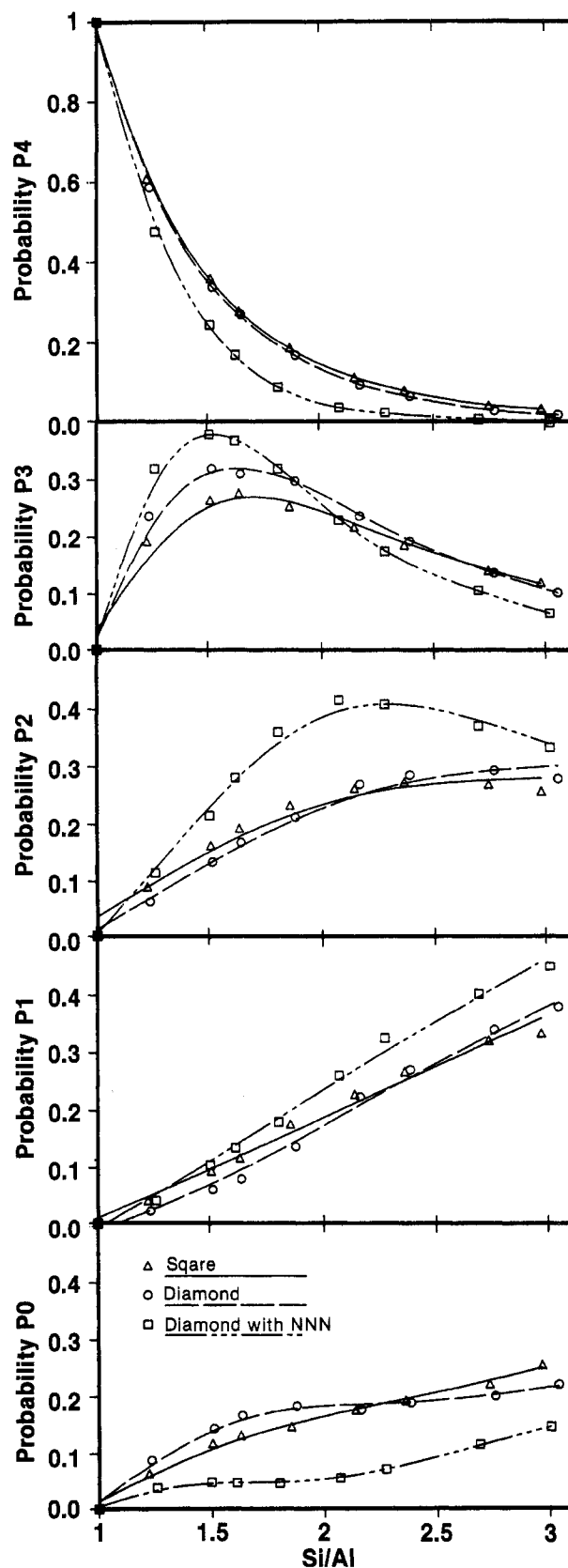

Figure 2. The distributions P_n of n alumina (n = 0, 1, 2, 3, 4) around a given Si vs. the ratio of Si over Al, for the 2-D square lattice with only nearest neighbors (nn), the 3-D diamond lattice with only nn, and the 3-D diamond with nn and nnn. In the last case $KT/J'_{Al-Al} = 2.5$.

It cannot find a good configuration; instead it gets caught in a local metastable state with $E > 0$ which is not of interest here.

One way to obtain better ground states was suggested by Kirkpatrick.[10] The idea is simply to start at $K_BT > |J_{Al-Al}|$ and
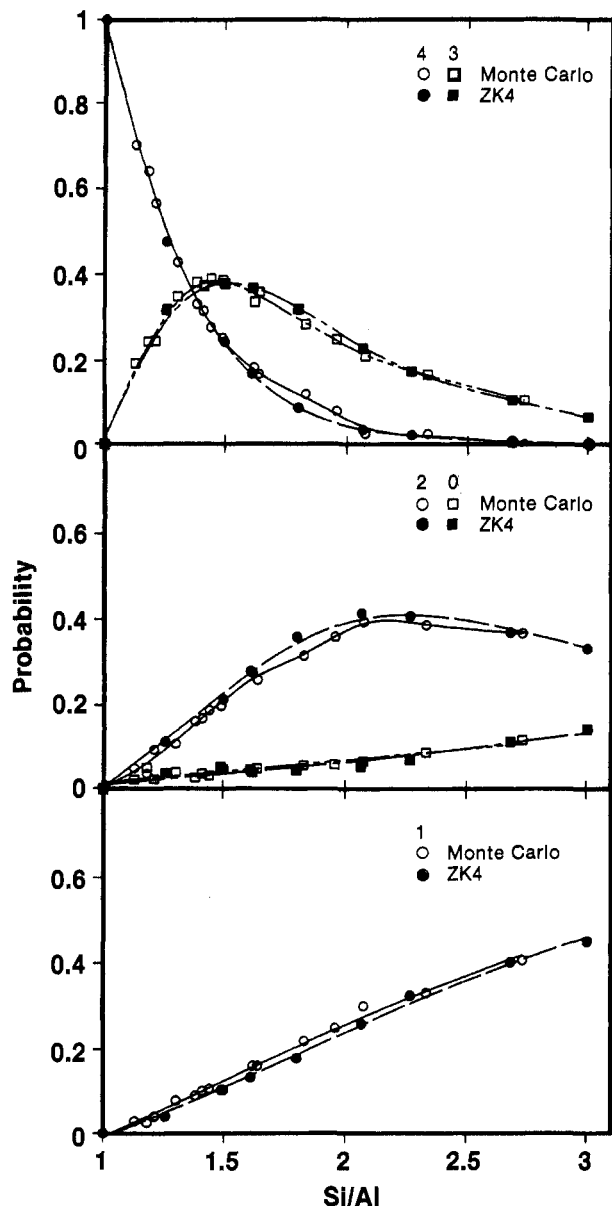
Figure 3. The distributions P_n of n alumina around a given Si vs. the ratio of Si over Al, for the ZK4 zeolite (solid symbols) and the Monte Carlo results for 3-D diamond lattice with nn and nnn (open symbols).

Figure 4. The distribution P_n of n alumina around a given Si vs. the ratio of Si over Al, for the faujasite zeolite (solid symbols) and the Monte Carlo results for 3-D diamond lattice with nn and nnn (open symbols). Here $J'_{Al-Al}/J_{Al-Al} = 0.07$ and $KT/J'_{Al-Al} = 3.0$.

slow cool the system with standard Monte Carlo finite temperature techniques. The final state of interest will of course be such that $K_B T \ll |J_{Al-Al}|$ but by slow cooling, the system will not get caught in a metastable state and can find good ground states with the proper probability distributions in this case with $N_{Al-Al} = 0$.

Our Monte Carlo simulations are based on the simple algorithm first introduced by Metropolis et al.[11] We randomly search the lattice and find an Al–Si nn pair and attemp to interchange them. If $\Delta E = E_f - E_i \leq 0$, that is the interchange lowered the energy, the interchange is accepted and the configuration with the atoms interchanged is used as the starting point for the next step. For $\Delta E > 0$, the new configuration is accepted based on the Boltzmann weight $P(\Delta E) = \exp(-\Delta E/K_B T)$. If $P(\Delta E) \geq x$, where x is a random number in the interval (0, 1) the interchange is accepted. If $P(\Delta E) \leq x$, the interchange is rejected and the original configuration is kept. By repeating this process many times, one simulates the thermal motion of the atoms in thermal contact with a heat bath at temperatures T. This particular choice of $P(\Delta E)$ ensures that we maintain detailed balance. For a complete review
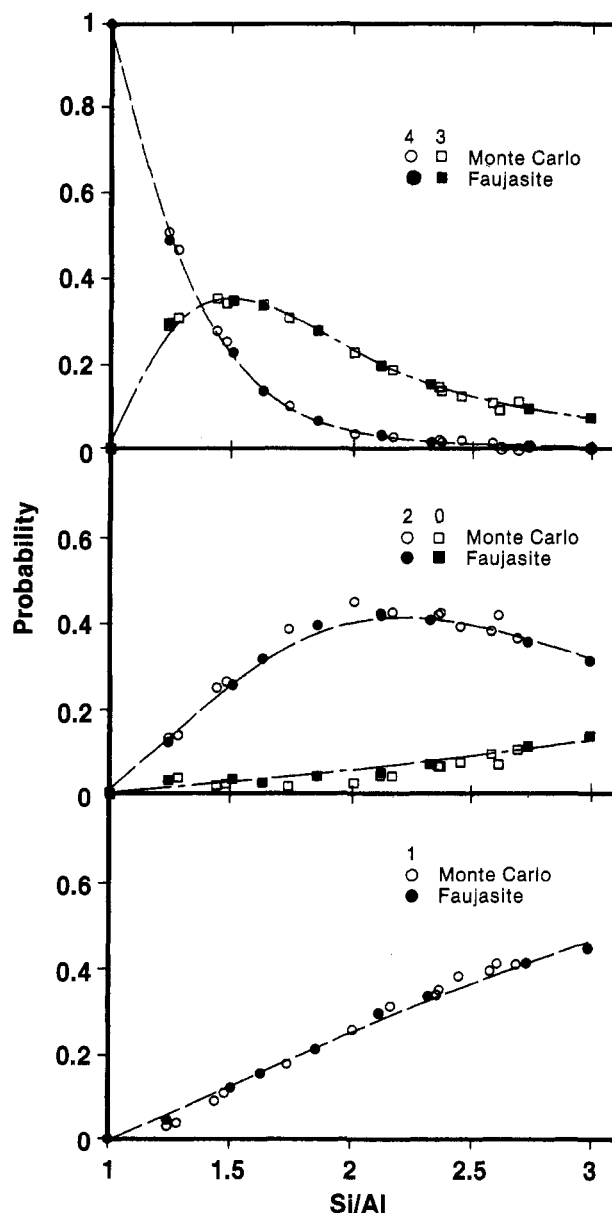
of Monte Carlo methods see Binder.[12]

Our simulations were done on lattices of size 100×100 for the 2-D square lattice and $20 \times 20 \times 20$ for the 3-D diamond lattice. We typically slow cooled the system using about 500–1000 Monte Carlo steps per atom (MCS), the larger number for the smaller values of R. As mentioned above, for large values of J_{Al-Al} the final system is actually athermal. However, in order to find good equilibrium ground states, we slow cooled the system from $K_B T \geq |J_{Al-Al}|$ to $K_B T \ll |J_{Al-Al}|$. The results of the calculation are shown in Figure 2.

First we present our results for the 2-D square lattice with only nn intereactions. As we can see from Figure 2 there is qualitative agreement with the experiment for ZK4 which as we will discuss below agrees with the case of diamond lattice with nnn interactions. We attempted to obtain better agreement between this model and experiment by also studying the diamond lattice. However, as seen in Figure 2 the diamond lattice data for the probabilities P_n are actually closer to the square lattice results than that for the experimental data. This simply indicates that with only near-

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est-neighbor interactions the connectivity of the lattice does not play a very important role. We also considered temperatures T which were less than or comparable to $|J_{Al-Al}|$ in order to see if it was possible to improve the results with nn interactions only. This allowed some violation of Lowenstein's rule; we found that the results did not significantly improve the agreement with experiment. Instead, we have found it necessary to introduce additional intereactions which we will discuss in the next section.

Next-Nearest-Neighbor Interactions. While it is possible to introduce many types of additional interactions, we have discussed above the fact that the introduction of nearest-neighbor J_{Al-Si} or J_{Si-Si} interactions will have no effect on the distributions P_n when $|J_{Al-Al}| > (K_B T, J_{Al-Si}, J_{Si-Si})$. Therefore, we decided to include the possibility of next-nearest-neighbors interactions which will affect P_n, even when $|J_{Al-Al}| >> K_B T$. The Hamiltonian is now written as

$$H = -J_{Al,Al}\sum_{n,n}\delta_{n_i,Al}\delta_{n_j,Al} - J'_{Al,Al}\sum_{nnn}\delta_{n_i,Al}\delta_{n_j,Al} \qquad (7)$$

where J'_{Al-Al} is the nnn Al–Al interaction which we choose to be repulsive, $J'_{Al-Al} \leq 0$. The second term in eq 7 is over all nnn pairs. Of course, we must have $|J'_{Al-Al}| << |J_{Al-Al}|$, in order not to violate Lowenstein's rule. Now the model has two parameter J_{Al-Al}/J'_{Al-Al} and $K_B T/J'_{Al-Al}$. For temperatures in the regime $|J'_{Al-Al}| << K_B T << |J_{Al-Al}|$, the nnn interactions are irrelevant and we obtain the results discussed above for nn interactions only. For lower temperatures, J'_{Al-Al} becomes important and P_n is changed. For $K_B T \leq |J'_{Al-Al}|$, then we find Lowenstein's rule is always obeyed for $J'_{Al-Al}/J_{Al-Al} \leq 0.05$. This can be considered as an asymptotic regime. Here, we will consider the final temperature T as the formation of the zeolites and it will affect the final distributions P_n. As in the nn case above, we always start our simulation at high temperature and slow cool to the final temperature in order to obtain the lowest free energy state.

We found it not possible to obtain results for all the P_n's that agree quantitatively with experiments for the 2-D square lattice, even with the two parameters. However, we were more successful for the diamond lattice, as shown in Figures 3 and 4. We obtained the results shown in Figure 3 for any $J'_{Al-Al}/J_{Al-Al} \leq 0.05$, i.e., in the asymptotic regime and temperature $K_B T/J'_{Al-Al} = 2.5$. The agreement between the numerical simulations of the 3-D diamond lattice and the experimental results for ZK4[7] is exceptional for all the probabilities P_n (see Figure 3). Note that if we stay in the asymptotic regime, the only parameter that we have in our problem is $K_B T/|J'_{Al-Al}|$, i.e., the ratio of the formation temperature T of the zeolite over the strength the nnn interaction. We found that it was very difficult to fit equally well the faujasite data by

only changing the parameter $K_B T/|J'_{Al-Al}|$. However, by changing the other parameter J'_{Al-Al}/J_{Al-Al} we could manage to fit the faujasite data as good as that for ZK4. In particular, we choose the parameter $J'_{Al-Al}/J_{Al-Al} = 0.07$ and $K_B T/|J'_{Al-Al}| = 3.0$ for the faujasite case. For $J'_{Al-Al}/J_{Al-Al} = 0.07$ we have a 1–3% violation of the Lowenstein rule in the whole R region. This violation is very difficult to see experimentally. The results for the faujasite case are shown in Figure 4. The agreement between numerical work (open symbols) and experimental work on faujasites[7] (solid points) is again impressive. We want to emphasize the point that we only have one parameter (KT/J'_{Al-Al}) in the ZK4 case and two $(kT/J'_{Al-Al}, J'_{Al-Al}/J_{Al-Al})$ in the faujasite and can fit all five possibilities P_n ($n = 0, 1, 2, 3, 4$) in the whole R region reasonably well. Therefore we believe that although we are using the diamond lattice instead of the real lattices for ZK4 and Faujasite zeolites, the underlying mechanism is the introduction of the nnn interactions. If we were to do the Monte Carlo simulations for the real lattices we believe that the experimental data could also be fitted equally well, the only difference will be the value of the parameter $K_B T/J'_{Al-Al}$.

Conclusions

We have performed numerical simulations on the 2-D square lattice and 3-D diamond lattice with nearest-neighbor and next-nearest-neighbors Al–Al interactions, in order to determine aluminum and silicon distributions in zeolites. Although our numerical simulations were done not on the real ZK4 or Faujasite structure, we believe that the diamond lattice with its underlying connectivity represents very well, as our results suggest, the real structures. We find that Lowenstein's rule with nearest-neighbor Al–Al interaction is sufficient to *qualitatively* explain the experimental data on the distributions P_n of n alumina around a given Si. To get a *quantitative* agreement with experimental data, the introduction of nnn Al–Al in the diamond lattice only is also necessary. Our simulations, for the first time, suggest that the distributions P_n are functions of the zeolite synthesis temperature. It is also predicted that the temperature dependence of P_n for ZK4 and Faujasite zeolites are different. It is very interesting to check experimentally these last two predictions of the numerical simulations. In particular, it is possible to form zeolites in higher temperatures and therefore offer a unique way of controlling the atomic distributions of zeolites and therefore control their catalytic behavior.